

## Electrochemical Preparation and Characterization of Fe-Cu Alloy on Anodized Alumina Templates

R. K. PATHAK<sup>1</sup> and PRIYANKA WAGELA<sup>2</sup>

<sup>1</sup>Department of Chemistry,  
Govt. MLB College, Indore, M.P., INDIA.

<sup>2</sup>Department of Eng. Chemistry,  
Vikrant Inst. of Tech. & Mang. Indore, M.P., INDIA.

(Received on: July 31, 2013)

### ABSTRACT

We have successfully deposited nano structured Fe-Cu alloy inside anodic aluminum oxide (AAO) templates from aqueous electrolyte containing Iron sulfate, Copper sulphate and Boric acid by using electrochemical methods. polarization curves, electrochemical impedance spectroscopy(EIS), the corrosion behavior of the Iron-copper nanocomposite coatings were examined. The corrosion parameters determined from the polarization curves recorded in 0.5M NaCl solution at room temperature. The surface morphology of deposited films was investigated by scanning electron microscopy (SEM). The compositional analysis of electrodeposited films was investigated by Energy dispersive X-ray spectroscopy (EDAX).

**Keywords:** Electrodeposition, Electrochemical Impedance spectroscopy (EIS), Corrosion rate (CR), Scanning Electron Microscope (SEM), Energy dispersive X-ray Analysis (EDAX).

### INTRODUCTION

Alloy electrodeposition is widely used in the production of new materials that require specific mechanical, chemical, and physical properties. This technique has been demonstrated to be very convenient because of its simplicity and low cost in comparison with other methods, such as mechanical alloying, sputtering, and vapour deposition.

The electrodeposition method is suitable for producing reproducible electrodeposited films at the same conditions. The objective of this study is to electrodeposits Fe-Cu alloy coatings onto anodized aluminum film and the corrosion behavior of Fe-Cu alloy deposits on anodized aluminum evaluated in comparison to the corresponding pure Fe and Cu coating. The composition and structure of these alloys were investigated.

The aim of this study is to investigate the corrosion behavior of electrodeposited Fe-Cu alloy undergoing a long-term immersion test in aerated NaCl aqueous solutions in order to improve the understanding of the corrosion mechanism of these layers in an aqueous medium. The experimental correlation between the operational electrodeposition parameters of Fe-Cu alloys, such as deposition current density and plating solution composition, coating morphology, coating composition and the corrosion resistance properties were

evaluated. Copper and Iron coatings were also studied under the same conditions for comparative purposes. The corrosion behavior of the two different types of Al<sub>2</sub>O<sub>3</sub>-copper nanocomposite coatings was examined using electrochemical methods such as polarization measurements and electrochemical impedance spectroscopy. The micro structural and composition analysis of the electrodeposited thin films were performed by Scanning Electron Microscopy and Energy Dispersive x-ray Analysis.

**TABLE I: The Solution composition and operating parameters for Fe-Cu Alloy**

Composition of solution	I	II	III	IV
FeSO <sub>4</sub> .7H <sub>2</sub> O	0.1 M	-	0.1M	0.1M
	2.7802 g	-	2.7802 g	2.7802 g
CuSO <sub>4</sub> .7H <sub>2</sub> O	-	0.1 M	0.1 M	0.01 M
	-	2.4978 g	2.4978 g	0.2496 g
H <sub>3</sub> BO <sub>3</sub>	4.5 g	4.5 g	4.5 g	4.5 g
Solution pH	4.5	4.5	4.5	4.5
Temperature (°C)	50	50	50	50
Time (sec)	30	30	30	30
Frequency (Hz)	200	200	200	200
Voltage (V)	19	19	19	19

## EXPERIMENTAL METHODS

The Aluminum samples were electro polished by electropolishing solution and rinsed with deionised water then samples were treated in 20% H<sub>2</sub>SO<sub>4</sub> for 1 min to remove any adherent oxide layer present on the surface. Finally, the samples were again washed in deionised water. This procedure was repeated until a clean and smooth surface was obtained. The electro-polished specimen was oxidized anodically in 10% oxalic acid at 30 volts DC for one hour using

lead as counter electrode. The temperature of the anodizing bath was maintained at  $24 \pm 0.5^\circ\text{C}$  by circulating chilled water through titanium cooling coil immersed in the solution. The pores formed during anodization were widened by dipping for 30 minutes at  $37 \pm 0.5^\circ\text{C}$  in 0.1M phosphoric acid. Iron & Copper was deposited inside these pores from an aqueous electrolyte containing Iron sulphate (0.1 M) and Copper sulphate (0.1 & 0.01 M) by applying high frequency (200 Hz) alternating current. After electrodeposition, the oxide layer was

removed partially in 0.5 M phosphoric acid at 87°C for 15 seconds to expose the shape of Iron-copper deposited on the porous AAO templates. All the electrolytes were prepared from Merck pre-analysis grade chemicals and distilled water. All electrochemical experiments and the deposition processes were carried out in a standard three electrode electrochemical cell equipped with platinum net as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. Fe-Cu alloy were obtained by electrodeposition from the solutions shown in Table I.

Energy dispersive analysis using X-rays (EDAX) was used to analyze the distribution of the elements in the final deposit. The surface morphology and the microstructure of the coating were analyzed using scanning electron microscopy (SEM)

with the help of Hitachi S-2500 Delta scanning electron microscope. Surface analysis used a LEICA S 440 scanning electron microscope with an attached energy dispersive X-ray analyzer.

A variety of electrochemical techniques including linear and Tafel polarization were used to evaluate the barrier resistance properties of the coating. The electrochemical characterization was done using an EG&G PAR model 273A potentiostat/galvanostat interfaced with a computer and a three-electrode setup. All depositions were carried out potentiostatically at -0.73 V vs. SCE.

Impedance behaviors of Fe-Cu alloy deposits were studied by electrochemical impedance spectra (EIS) in the frequency range from 100 KHz to 100 MHz.

**TABLE II: Corrosion parameter of Fe-Cu alloy deposit in different concentration**

Constitute	Concentration of deposit (M)	$E_{\text{corr}}$ (V v/s SCE)	(V v/s SCE)	$\beta_a$	$\beta_b$	$I_{\text{corr}}$	$R_p$	Corrosion Rate
		Obs	Cal	(V/dec)	(V/dec)	(A/cm <sup>2</sup> )	(Ohm)	(mm/yr)
Cu	0.1	-.711	-.704	.193	.109	6.096e-6	1.909e+3	7.068e-2
Fe	0.1	-.693	-.715	.12	.149	1.703e-6	5.829e+3	1.98e-2
Cu-Fe	0.1 : 0.1	-.745	-.74	.095	.026	1.73e-6	7.921e+2	2.011e-2
Cu-Fe	0.01 : 0.1	-1.059	-1.056	.144	.138	4.517e-8	2.44e+5	5.25e-4

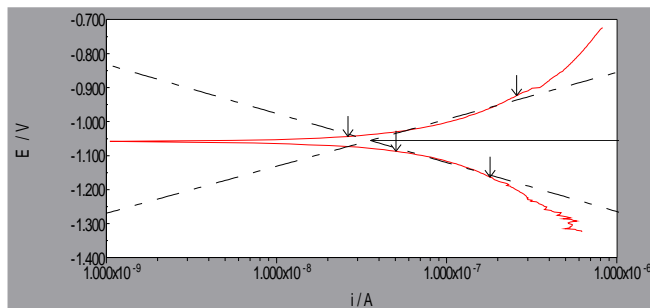
## RESULTS AND DISCUSSION

The corrosion behaviour of electrodeposited Fe-Cu alloy under different concentration and compared it with pure Iron and Copper at optimum frequency and average current density was evaluated using Tafel polarization method. Electroplated specimens were subjected to corrosion study

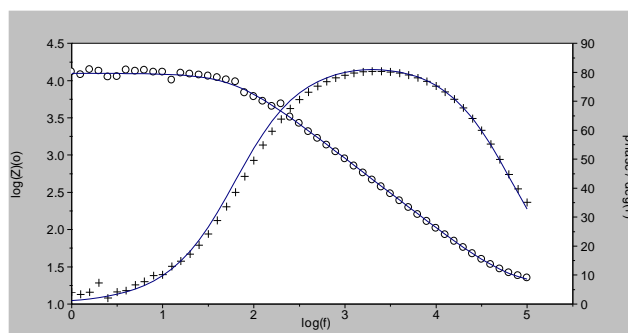
in aerated 0.5 M NaCl solution and experimental data are given in Table 2. Corrosion rates of the deposits were determined by Tafel's extrapolation method. A representative Tafel plot for 0.1 M Fe and 0.1 M Cu is shown in fig 1. The polarization studies have been made at scan rate of 1 mV/s in a potential ramp of 0.73 V from OCP. Observed  $E_{\text{corr}}$  and Tafel's slopes

at different current densities are shown in Table 2. The corrosion rates obtained from the polarization plots for Fe-Cu alloy coating are compared in Table 2 with those of Iron and Copper in the corroding solution. The values of Tafel slope indicate that the corrosion rate is controlled more by cathodic

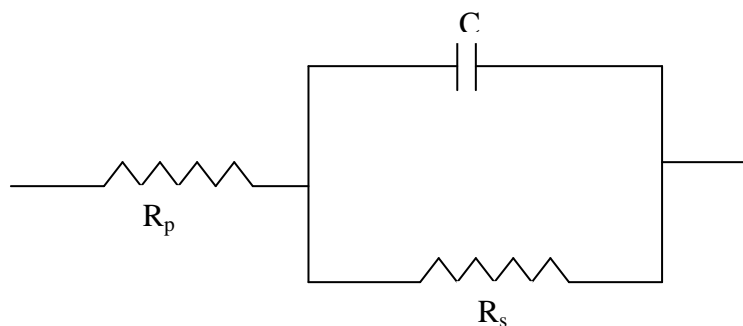
reaction. Observed results showed that, the corrosion rate of Cu is high in compare to Fe. Fe-Cu alloy at  $1.73 \times 10^{-6}$  having about 0.1 M Cu and 0.1 M Fe was found to show least corrosion rate. The corrosion results indicate that pure iron coating is more corrosion resistance.



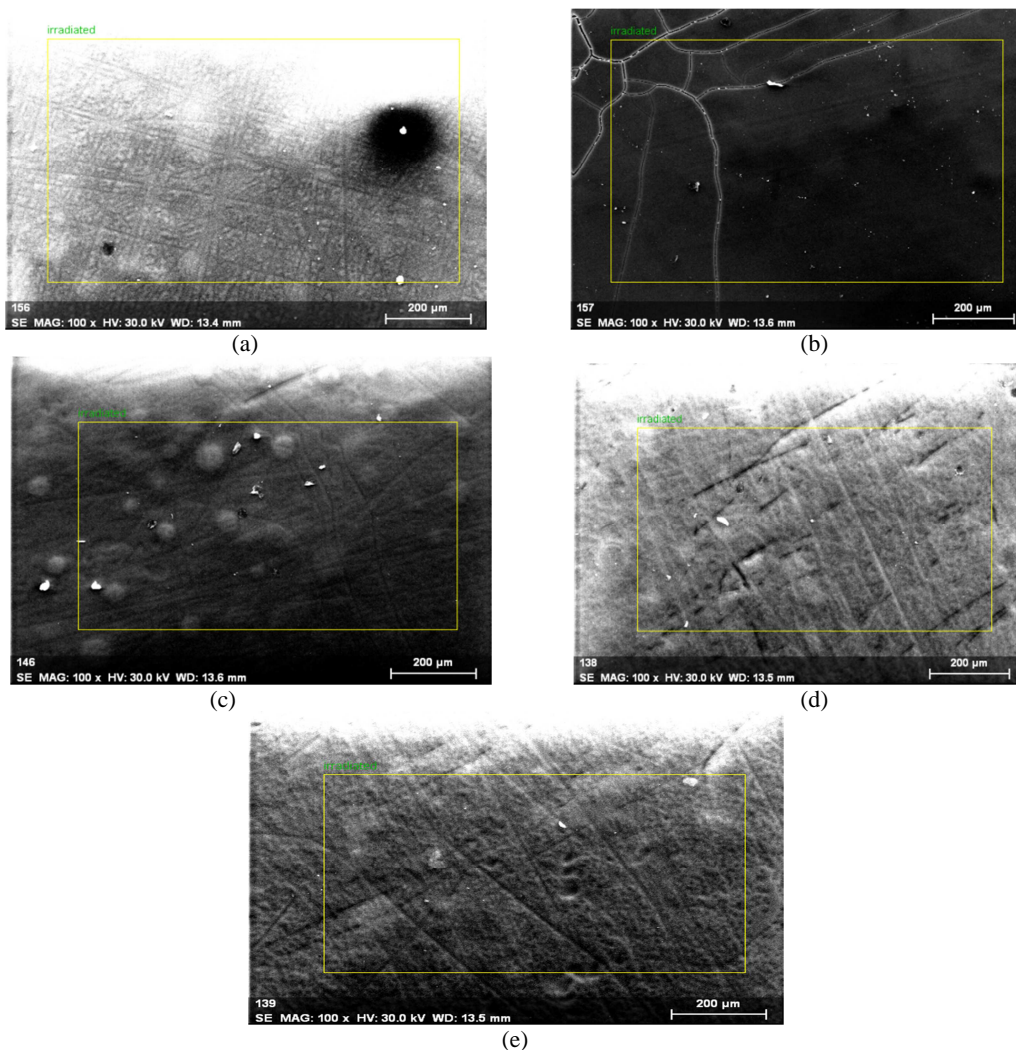
**Fig. 1. Tafel Plot of 0.1M Fe & 0.01 M Cu.**



**Fig. 2. Bode plot of 0.1 M Fe**



**Fig. 3: Electrical equivalent of electrified interface of Fe-Cu alloy deposited**



**Fig. 4: SEM image of Fe-Cu alloy deposit at different concentration**

(a) 0.1M Fe      (b) 0.1M Cu      (c) 0.1 M Fe & 0.1 M Cu      (d) Unetched 0.1M Fe & 0.01 M Cu  
 (e) Etched 0.1 M Fe & 0.01 M Cu

The electrochemical behaviours of electrodeposited Fe-Cu alloys were studied using impedance spectroscopy. EIS was used to evaluate the barrier properties of the coatings and determine the polarization resistance and the corrosion rates without

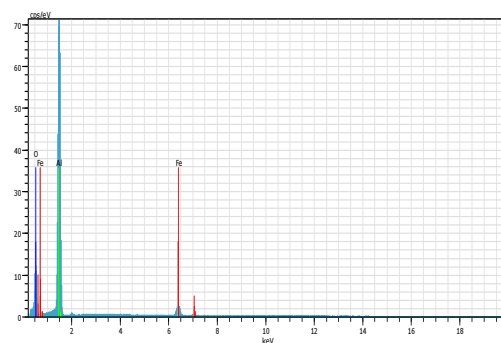
modifying the surface. A Bode plot of Fe-Cu alloy deposits is given in fig 2. The solution resistance remains the same for all deposits. The electrical equivalent of the electrified double layer for optimized equivalent of the electrified double layer for optimized

deposit is given in the fig.3. The EIS data obtained using  $R_s (Q_{dl} R_p)$  and  $R_s (Q_{dl} R_p W)$  Circuit where, ( $R_s$ ) is the solution resistance, ( $Q_{dl}$ ) is the constant phase element for electrical double layer; ( $R_p$ ) is the polarization resistance and ( $W$ ) diffusion resistance element known as Warburg impedance, is due to the influence of diffusion of the oxidants and reductants on the overall reaction rate.  $R_p$  values can be approximately determined by fitting the bode plot to a simple equivalent circuit consisting of ohmic resistance, double layer capacitance, and polarization resistance. The equivalent circuit is shown in fig 3. The parameters for the C.P.E. element are a flexible capacitor,  $Q$  and an exponent  $n$ . Since the C.P.E. is only a true capacitor where the exponent  $n$  is unity. Bode plots are not found to be perfect as expected from the theory of EIS for the assumed equivalent circuit, and this difference can be explained as the plots obtained in the real system represent a general behaviour where the double layer on the interface of the metal/solution does not behave as a real capacitor.

Scanning Electron Microscopy was used for the microstructural characterization and the composition analysis. These investigation are limited by resolution of the SEM, satisfactory quality of SEM image was possible when the thickness of single Fe-Cu alloy layer exceeds-300 $\mu$ . Based on SEM investigation high efficiency of the deposited thickness measured by SEM was similar to that predicted from deposition charge. The variation in the surface morphology of the deposit with concentration difference is shown in fig 4.

Energy dispersive x-ray (EDX) analysis was carried out on both the locations for identifying the constituents present in the deposit. It was found that both iron and copper were present through out the deposit. Variation of iron and copper concentrations in both these deposits were calculated by EDX analysis and the data is given in Table 3. EDX spectrum shows the presence of aluminum and oxygen which are from the base substrate and its conversion to aluminum oxide. Compositional changes along the surface are due to in homogeneities on the porous aluminum oxide surface resulting in non uniform current distribution.

EDAX was used to analysis the Fe-Cu ratio of the electrodeposits. To ensure accuracy of the element distributions EDAX analysis was done at several points on the surface of the substrate. The concentration of the constituent elements was determined by comparing the intensities of the X-ray spectrum to the standard intensities of the pure element. The EDAX images are shown in fig 5.



**Fig. 5(a): EDAX image of 0.1 M Fe film**

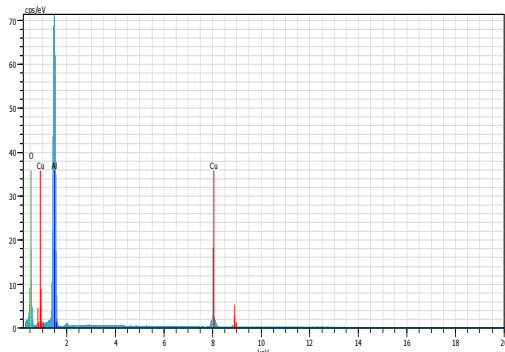


Fig. 5(b): EDAX image of 0.1 M Cu film

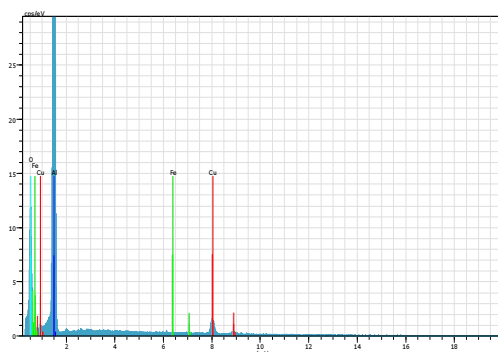


Fig.5(c): EDAX image of 0.1 Cu &amp; 0.1 M Fe film

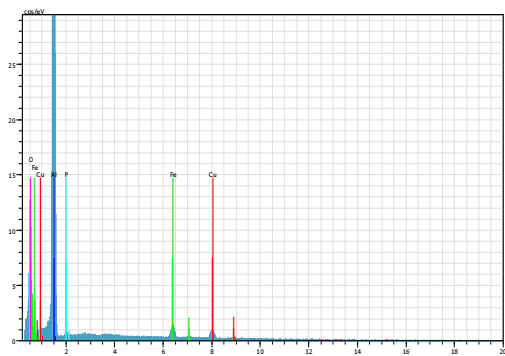


Fig.5(d):EDAX image of Unetched 0.01 Cu &amp; 0.1 M Fe film

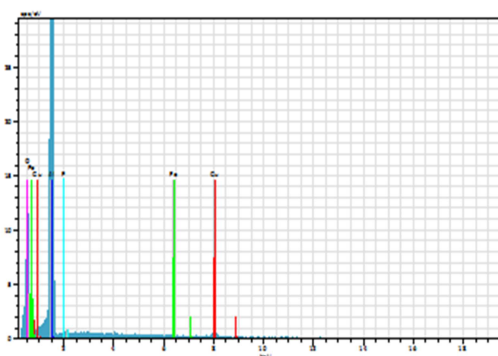


Fig. 5(e): EDAX image of Etched 0.01 Cu &amp; 0.1 M Fe film

Table III. Dependence of composition on Fe-Cu alloy concentration

Sample	Fe-Cu alloy (M)	Fe (Atomic Weight %)	Cu (Atomic Weight %)	Al (Atomic Weight %)
1	Fe- 0.1	2.73	-	37.85
2	Cu- 0.1:0.1	-	3.29	39.10
3	Fe-Cu:: 0.1 :0.1	0.16	2.17	38.22
4	Fe-Cu:: 0.1: 0.01 (Unetched)	1.58	1.40	35.83
5	Fe-Cu:: 0.1: 0.01 (Etched)	0.28	1.15	37.73

## CONCLUSION

Effective control of the iron-copper ratio in composite alloy coating was achieved in the presence of small amount of

$\text{H}_3\text{BO}_3$ . The homogeneous and smooth Fe-Cu alloys were electrodeposited on steel at different concentration. Chemical composition of Fe-Cu alloys was determined by EDX analysis. The corrosion properties

of Fe-Cu alloys were investigated. The influence of the plating current density in Fe-Cu alloys electrodeposition on the corrosion resistance of these alloys was shown. It was obtained that Fe-Cu alloy deposited at Cu 0.1M and Fe 0.1 M exhibited the lowest corrosion rate. Polarization studies on these deposits show a large reduction in the corrosion current of these alloy compared to pure Copper.

### ACKNOWLEDGEMENT

The authors are grateful to RRCAT Indore for instrumental analysis. The Authors would also like to thanks to Mr. P Ramshankar.

### REFERENCES

1. Bard A.J., Electrochemical methods. Fundamentals and applications, New York, John Wiley and Sons, (2001).
2. Brenner A., Electrodeposition of alloys, New York, Academic Press, 1 (1963).
3. Chiang K. Mintz T., Gravimetric techniques. Techniques for corrosion monitoring, Cambridge England. Woodhead Pub. Ltd. 247, (2008).
4. Fratesi R. Roventi G. Electrodeposition of Zinc- Nickel coatings from a chloride bath containing, *J. Appl. Electrochem.* 22, 657, (1992).
5. Paunovic M. Schlesinger M. Fundamental considerations. Modern electroplating., 4<sup>th</sup> ed. New york. John Wiley and Sons. (2000).
6. Macdonald J.R. Impedance spectroscopy, Wiley Interscience, New York (1987).
7. Gabrielli C. Electrochemical impedance Spectroscopy, Principles, Instrumentation and applications. Physical electrochemistry, ed. I, Rubinstein, Marcel Dekker, Inc, 243 (1995).
8. Mahalingam T. Kathalingam A. Studies of electrosynthesised Zinc selenide thin films. *J. New Mat.Electrochem. Sys.* 10, 15 (2007).
9. Karahan I H. Electrodeposition and properties of ZnFeNi alloys, *Chinese J Physics*, 46, 1 (2008).
10. Thangaraj V. Udayshankar N K., Development of Zn-Co alloy coating by pulsed current from chloride bath, Ind., *J. Chem. Tech.* 15, 581 (2008).
11. Pathak R. K., Electrosynthesis and characterization of CdSeHgTl thin films. *Res. J. Chem. Sc.* 3 (4) 44 (2013).